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Low temperature vibrational spectroscopy. III. Structural aspects and detection of phase transitions in crystalline alkali metal and tetramethylammonium hexabromotellurates and platinates

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The low-frequency infrared and Raman spectra of $A_2[TeBr_6]$ with $A = K, Rb, Cs, NH_4, (CH_3)_4N, (CD_3)_4N$ and of $A_2[PtBr_6]$ with $A = K, (CH_3)_4N, (CD_3)_4N$ were recorded as a function of temperature down to ~ 100 K. The spectra of the Rb and Cs compounds changed little. For the other salts new, and in some cases sharp, bands were observed at low temperatures. The spectra have been assigned, and in most cases a confirmation of previous results was obtained. The assignment ambiguity in the literature on the ν_4 mode of $[PtBr_6]^{2-}$ has been solved, placing it at ~ 130 cm^{-1} . The majority of the new low temperature bands were interpreted in accordance with the known occurrence of phase transitions breaking the ideal antiferroite $K_2[PtCl_6]$ -type symmetry, but it appears that the method of vibrational spectroscopy does not invariably reflect the presence of phases of lower symmetry. In the spectra of the tetramethylammonium compounds, methyl torsional IR bands were observed with increasing sharpness at lower temperatures. This behavior can be correlated with a gradual ordering of methyl torsional disorder. The potential energy barrier against methyl group rotation was found to be of the order 4–5 kcal/mol, showing that the methyl groups are not pseudo freely rotating. The anharmonicity of the vibrations in tetramethylammonium hexabromotellurate seems to increase abnormally at lower temperatures, possibly due to enhanced methyl–bromine interaction.

I. INTRODUCTION

The application of temperature dependent vibrational spectroscopy has proved to be a practicable way to detect new phase transitions in solids. Equipment for variable temperature spectroscopy is common nowadays, and exploratory survey experiments can be quickly carried out using powder samples. We have previously used this approach¹ to examine some hexachlorometalate (IV) salts. Having examined some hexachlorotellurates, -platinates, and -stannates at lower temperatures, we here consider as further examples simple hexabromotellurates and hexabromoplatinates $A_2(MBr_6)$, with $A = K, (CH_3)_4N, (CD_3)_4N$ for $M = Te$ and Pt , and $A = Rb, Cs, NH_4$ for $M = Te$ only.

The tellurium bromides have previously been examined by x-ray structural,^{2–5} ^{79}Br nuclear quadrupole resonance,⁶ and ^{125}Te Mössbauer⁷ methods. The NQR data⁶ indicated nonequivalent bromine atoms for monoclinic $K_2(TeBr_6)$ crystals already at room temperature and for $(NH_4)_2(TeBr_6)$ below $-52^\circ C$, whereas the Cs and $(CH_3)_4N$ salts have equivalent bromine atoms at room temperature and down to liquid–nitrogen temperature. For all $A_2(TeBr_6)$ compounds examined so far, no indication has been found of any Gillespie type distortion of the regular $(TeBr_6)^{2-}$ octahedra due to the presence of the $5s^2$ lone pair of electrons. We wanted to investigate whether such effects or phase transitions could be observed at low temperatures using IR and Raman spectroscopy. Furthermore, it has recently been shown by x-ray diffraction⁸ that Te takes a $S_6 \equiv \bar{3}$ site symmetry in the cubic $[(CH_3)_4N]_2(TeBr_6)$ crystals (space group $Fd\bar{3}c \equiv O_h^h$, $Z = 32$), and an investigation of the influence of this lower symmetry on the spectra was a motivation for this study.

The $K_2(PtBr_6)$ compound has been investigated previously by several techniques, but this is not the case with $[(CH_3)_4N]_2(PtBr_6)$. At room temperature, $K_2(PtBr_6)$ has the cubic antiferroite structure.^{9–11} As the temperature is decreased, it exhibits several structural phase transitions.^{12–14} The influence of this complicated behavior on the vibrational spectra is unknown and hence we decided to investigate $K_2(PtBr_6)$. The tetramethylammonium hexabromoplatinate salts were included with the intention of comparing to the tellurates. The rubidium, cesium, and ammonium salts were left out, since they are known to remain cubic down to liquid–nitrogen temperature^{15,16} [$(NH_4)_2(PtBr_6)$ has a transition at 58 K].

II. STRUCTURES, SELECTION RULES, AND SPECTROSCOPIC WORK

A. $K_2(TeBr_6)$

The room temperature structure of the potassium salt is accurately known² (see Fig. 1). It is monoclinic ($P2_1/n \equiv C_{2h}^5$, $Z = 2$) due to small rotations of virtually undistorted $(TeBr_6)^{2-}$ octahedra in a pseudo- $K_2(PtCl_6)$ antiferroite lattice, as also discussed in Ref. 1. At higher temperatures, a real $K_2(PtCl_6)$ -type structure for $K_2(TeBr_6)$ probably exists; evidence of phase transitions at ~ 405 and ~ 434 K has been found by differential thermal analysis,¹⁴ and perhaps a further transition takes place at ~ 243 K.⁶ However, based on x-ray powder diffraction data, Fergusson and Heweltdt⁵ claimed that $K_2(TeBr_6)$ was cubic at room temperature, but this is probably due to low accuracy (these authors apparently did not know Brown's single crystal results).²

The infrared and Raman spectra of $K_2(TeBr_6)$ have been obtained at room temperature,^{17–22} and in IR at

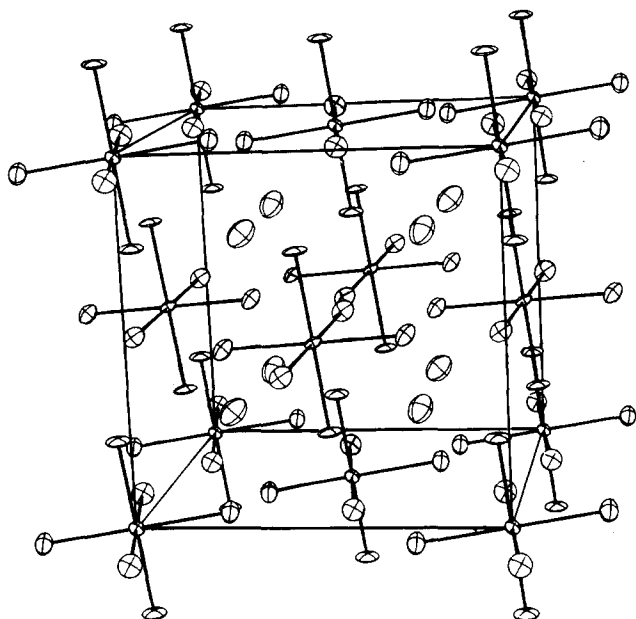


FIG. 1. The structure of $K_2(TeBr_6)$ as determined by Brown,² showing an unconventional doubled cell which is most convenient when comparing with the $K_2(PtCl_6)$ standard structure.

~120 K.²⁰ Selection rules (factor group analysis) based on the monoclinic structure are summarized in Table I.

B. $(Rb, Cs, NH_4)_2(TeBr_6)$

These salts seem to crystallize in the $K_2(PtCl_6)$ lattice. For Rb, the evidence is less convincing (powder x-ray,⁵ Mössbauer,⁷ IR, and Raman data¹⁹⁻²¹), but for Cs, little doubt exists (single crystal³ and powder^{4,5} x-ray data and other kinds of evidence^{6,7,18-21,23}). At room temperature, the ammonium salt has the same structure too.^{3,5} At lower temperatures, probably below 214 K [according to DTA (differential thermal analysis)¹⁴] or 221 K (according to NQR data⁶), another phase exists. The tetragonal space group $P4/mnc \equiv D_{4h}^6$ (No. 128 with $Z=2$) was deduced from single crystal x-ray film data.³ The phase transition is reversible and there is evidence of yet a third phase at temperatures below ~200 K (NQR⁶), or below 194 K (DTA¹⁴).

The selection rules resulting from the $K_2(PtCl_6)$ structure have often been given, e.g., in Ref. 1. For the $(NH_4)_2(TeBr_6)$ low temperature phase of D_{4h}^6 symmetry,

TABLE I. Unit cell group analysis^a of $K_2(TeBr_6)$ of space group C_{2h}^5 ($\equiv P2_1/n$, No. 14, $Z=2$). Te is on Wyckoff site a (C_i symmetry); Br is on sites of type c with no symmetry.²

C_{2h} symmetry	T_A	T^b	$R(TeBr_6)$	$N_i(TeBr_6)^b$	Activity in
A_g		$3(\nu_{L2})$	$3(\nu_{L1})$	$6(\nu_1 + 2\nu_2 + 3\nu_3)$	Raman
B_g		$3(\nu_{L2})$	$3(\nu_{L1})$	$6(\nu_1 + 2\nu_2 + 3\nu_3)$	Raman
A_u	1	$5(\nu_{L3})$		$9(3\nu_3 + 3\nu_4 + 3\nu_5)$	IR
B_u	2	$4(\nu_{L3})$		$9(3\nu_3 + 3\nu_4 + 3\nu_5)$	IR

^a T_A = inactive acoustic, T = optic-branch translatory, R = rotatory, and N_i = internal modes.

^bThe notation of the frequencies ν_1 – ν_{L3} refers to those of O_h symmetry.¹

they are less restrictive allowing for possible factor group doublings, splittings of the ν_1 – ν_5 modes and ν_6 IR activity.

C. $[(CH_3)_4N]_2(TeBr_6)$

This compound has a single ^{79}Br NQR line at room, dry ice, and liquid-nitrogen temperatures,⁶ but a powder x-ray diffraction pattern quite different from that of a $K_2(PtCl_6)$ type structure.⁶ The compound was recently shown by single crystal x-ray diffractometry⁸ to have an eightfold increased cubic unit cell of space group $Fd3c \equiv O_h^8$ (No. 228) with $Z=32$ and $a=26.563$ Å. The $(TeBr_6)^{2-}$ ion is rotated 9.1° around $\{111\}$ -type vectors and slightly deformed towards a flattened trigonal antiprism; the 2.700 Å long Te–Br bonds form angles 7.4° with the cubic axes, and 89.2° or 90.8° with each other. There are two kinds of tetramethylammonium ions (Fig. 2). The deformation of $(TeBr_6)^{2-}$ has nothing to do with the $5s^2$ pair of electrons, since a similar deformation occurs in $[(CH_3)_4N]_2(PtCl_6)$.

The selection rules based on this structure are given in Table II. They predict a number of "factor group splittings" and IR activity of the formerly inactive ν_6 bending mode of $(TeBr_6)^{2-}$. The modes involving hydrogen are omitted except for the methyl torsions since we are primarily interested in the region below 600 cm^{-1} where the $(MX_6)^{2-}$ and the external modes occur. It has been shown that the only internal modes of the tetramethylammonium ion occurring within this range are the C_4N skeletal deformations ν_8^* and ν_{19}^* and the methyl torsions ν_4^* and ν_{12}^* ; and their approximate frequencies are known.²⁴ Adams and Morris¹⁹ have obtained the room temperature spectra and assigned the $(TeBr_6)^{2-}$ modes.

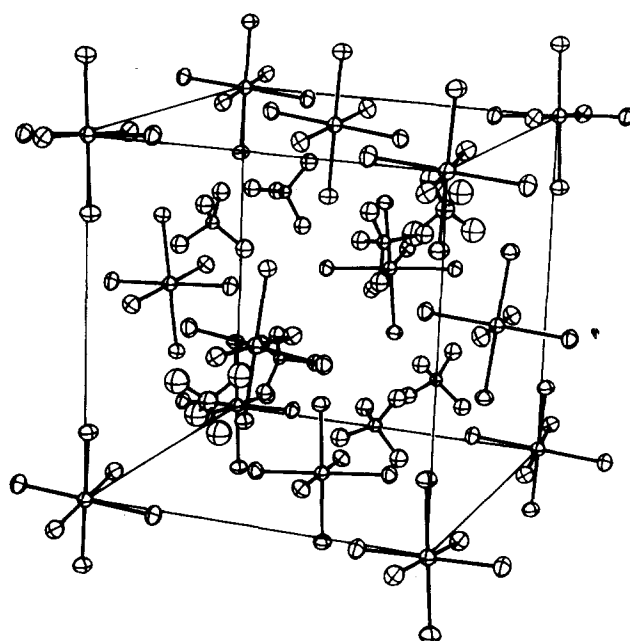


FIG. 2. The structure of $[(CH_3)_4N]_2(TeBr_6)$ as determined by Berg and Nielsen.⁸ Only 1/8 of the full cell is depicted.

TABLE II. Unit cell group analysis^a of $[(\text{CH}_3)_4\text{N}]_2(\text{TeBr}_6)$ of space group O_h^8 ($\equiv Fd3c$, No. 228, $Z=32$). Te is on Wyckoff site c (S_6 symmetry); Br is on site h (C_1), N on $a(T)$ and $d(S_4)$, and C on e (C_3) and $h(C_1)$.⁸

O_h symmetry	T_A	T	$R(\text{TeBr}_6)$	$R(\text{C}_4\text{N})$	$N_i(\text{TeBr}_6)$	$N_i(\text{C}_4\text{N})$	Methyltors ^b	Activity in
A_{1g}		1	1	1	$2(\nu_1 + \nu_5)$	$3(\nu_1' + \nu_1'' + \nu_5'')$	$2(\nu_4' + \nu_{12}'')$	Raman
A_{2g}		1	1	0	$2(\nu_1 + \nu_5)$	$4(\nu_1' + \nu_2'' + \nu_3'' + \nu_4'')$	$2(\nu_4' + \nu_{12}'')$	
E_g		1	2	1	$4(2\nu_2 + 2\nu_5)$	$7(2\nu_2' + \nu_1'' + 2\nu_2'' + \nu_3'' + \nu_4'')$	$2(\nu_4' + \nu_{12}'')$	Raman
T_{1g}		3	3	4	$6(\nu_1 + 2\nu_2 + 3\nu_5)$	$8(\nu_3' + \nu_4' + \nu_1'' + \nu_2'' + 2\nu_3'' + 2\nu_4'')$	$4(\nu_{12}' + 3\nu_{12}'')$	
T_{2g}		4	3	3	$6(\nu_1 + 2\nu_2 + 3\nu_5)$	$9(\nu_3' + \nu_4' + \nu_2'' + 3\nu_3'' + 3\nu_4'')$	$4(\nu_{12}' + \nu_{12}' + 2\nu_{12}'')$	Raman
A_{1u}		2	0	0	$3(\nu_3 + \nu_4 + \nu_6)$	$4(\nu_1' + \nu_2'' + \nu_3'' + \nu_4'')$	$2(\nu_4' + \nu_{12}'')$	
A_{2u}		1	0	1	$3(\nu_3 + \nu_4 + \nu_6)$	$3(\nu_1' + \nu_1'' + \nu_2'')$	$2(\nu_4' + \nu_{12}'')$	
E_u		3	0	1	$6(2\nu_3 + 2\nu_4 + 2\nu_6)$	$7(2\nu_2' + \nu_1'' + 2\nu_2'' + \nu_3'' + \nu_4'')$	$2(\nu_4'' + \nu_{12}'')$	
T_{1u}	1	6	0	3	$9(3\nu_3 + 3\nu_4 + 3\nu_6)$	$9(\nu_3' + \nu_4' + \nu_2'' + 3\nu_3'' + 3\nu_4'')$	$4(\nu_{12}' + \nu_{12}' + 2\nu_{12}'')$	IR
T_{2u}		6	0	4	$9(3\nu_3 + 3\nu_4 + 3\nu_6)$	$8(\nu_3' + \nu_4' + \nu_1'' + \nu_2'' + 2\nu_3'' + 2\nu_4'')$	$4(\nu_{12}' + 3\nu_{12}'')$	

^aFor explanation of symbols, see Table I. The distribution of the internal modes (Herzberg notation ν_i) was obtained using the correlation approach. ' and '' refers to tetramethylammonium ions on site a and d , respectively.

^b ν_4 and ν_{12} modes of $(\text{CH}_3)_4\text{N}$ are methyltorsions (see Ref. 17). Other hydrogen modes are left out because of their high frequencies.

D. $\text{K}_2(\text{PtBr}_6)$

Powder and single crystal x-ray examinations have shown that $\text{K}_2(\text{PtBr}_6)$ has the $\text{K}_2(\text{PtCl}_6)$ -type structure at room temperature.⁹⁻¹¹ According to the temperature variation of the data for the ^{79}Br NQR frequency and spin-lattice relaxation time, and data obtained by DTA,¹⁴ transitions occur in $\text{K}_2(\text{PtBr}_6)$ at 169, 143, 137, 105, and 78 K.¹³ It seemed from the analysis¹³ of the experiments that the crystal becomes tetragonal (symmetry class C_{4h}) in the range 169–143 K, possibly due to some finite reorientation of undistorted $(\text{PtBr}_6)^{2-}$ octahedra (perhaps a $\sim 7^\circ$ rotation¹⁵ around one of the cubic axes). The structure of the phase obtained between 143 and 137 K has a still lower symmetry, whereas NQR and x-ray results indicated a tetragonal structure again between 137 and 105 K.¹³

The infrared and Raman spectra have been recorded and analyzed in several reports,^{10,25-30} in some cases as a function of pressure,^{31,32} but not as a function of temperature.

E. $[(\text{CH}_3)_4\text{N}]_2(\text{PtBr}_6)$

The structure is unknown but presumably analogous to that of the tellurium compound. Two phases of the compound have been reported, a cubic one at room temperature with a density of 2.402 g/cm^3 (18°C) and another less symmetric one (pseudocubic) obtained at low temperatures in a polarizing microscope with liquid air cooling.³³ To our knowledge, the vibrational spectra have not been recorded even at room temperature.

III. EXPERIMENTAL

The tellurium compounds were prepared³⁴ by dissolving TeO_2 in hot concentrated hydrobromic acid and adding ABr [$A=\text{K}, \text{Rb}, \text{Cs}, (\text{CH}_3)_4\text{N}, (\text{CD}_3)_4\text{N}$] dissolved in a minimum of water. The orange to red crystals were separated and washed with a minimum of cold conc. HBr and dried at $\sim 80^\circ\text{C}$. The dark red platinum compounds were obtained from solutions of $\text{H}_2(\text{PtBr}_6)$ and ABr [$A=\text{K}, (\text{CH}_3)_4\text{N}$, and $(\text{CD}_3)_4\text{N}$] by slow evaporation. {Analyses by Volhard titration; K_2TeBr_6 : Br—found = 68.8%, calc = 69.97%; $[(\text{CH}_3)_4\text{N}]_2\text{TeBr}_6$: Br—found = 64.3%, calc = 63.46%}. The techniques used in

measuring the spectra have been described in detail.¹ The Raman spectra were obtained on powders, using ~ 20 to $\sim 80 \text{ mW}$ of the 647.1 nm Kr^+ laser line; the infrared spectra were calculated by Fourier transformation of interferograms, and care was exercised to determine the temperatures.¹ The spectral resolution was $2\text{--}4 \text{ cm}^{-1}$.

IV. RESULTS AND DISCUSSION

A. General

The spectra obtained for $\text{K}_2(\text{TeBr}_6)$, $\text{Cs}_2(\text{TeBr}_6)$, and $[(\text{CH}_3)_4\text{N}]_2(\text{TeBr}_6)$ are shown in Figs. 3 and 4; those for $\text{Rb}_2(\text{TeBr}_6)$ or $(\text{NH}_4)_2(\text{TeBr}_6)$ and $[(\text{CD}_3)_4\text{N}]_2(\text{TeBr}_6)$ were quite analogous to $\text{Cs}_2(\text{TeBr}_6)$ and $[(\text{CH}_3)_4\text{N}]_2(\text{TeBr}_6)$, respectively. Spectra of the hexabromoplatinates are given in Fig. 5. Frequencies of all the observed bands are given in Table III.

Comparisons of spectra at room and low temperatures showed the usual sharpening and small shifts in band positions. Apart from this, the Rb and Cs salts changed very little. The other salts each have their own characteristic behavior.

B. Cubic compounds ($\text{Rb}, \text{Cs}, (\text{NH}_4)_2(\text{TeBr}_6)$)

The room temperature vibrational data given for these compounds in the literature were reproduced within $\sim 2 \text{ cm}^{-1}$.¹⁷⁻²³ The Raman active lattice mode ν_{L2} of $\text{Cs}_2(\text{TeBr}_6)$ was seen at 43 cm^{-1} and Stufkens²³ also had a weak feature near $\sim 45 \text{ cm}^{-1}$. The IR spectrum²⁰ of $\text{Cs}_2(\text{TeBr}_6)$ at $\sim 120 \text{ K}$ is in agreement with our results. The new low temperature data (Table III) is in accordance with the absence of phase transitions for Rb and Cs salts, whereas new IR bands appeared for $(\text{NH}_4)_2(\text{TeBr}_6)$, presumably due to the known phase transitions near 200 K .^{6,14} The assignments given tentatively in Table III follow those of $\text{K}_2(\text{TeBr}_6)$ (see Sec. IV C).

The IR active modes ν_4 and ν_{L3} both have the same T_{1u} symmetry and thus may couple. This might explain the peculiar behavior of the band formally assigned as the lattice mode ν_{L3} . Note that $\nu_{L3}(\text{Rb}) \leq \nu_{L3}(\text{Cs})$, even though the mass of rubidium is much less than that of cesium.

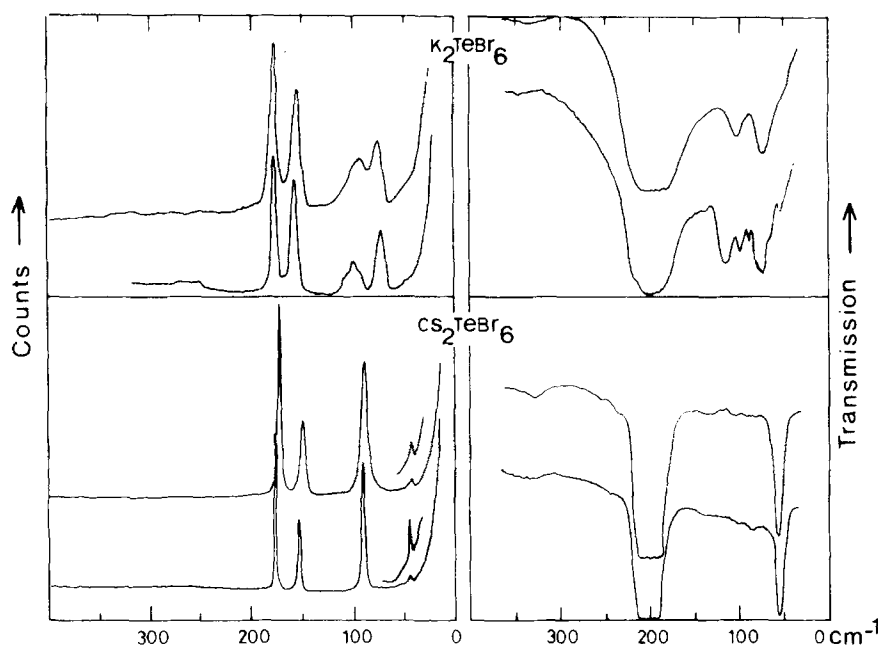


FIG. 3. $K_2(TeBr_6)$ and $Cs_2(TeBr_6)$: Raman (left) and far IR spectra of powder samples,¹ at room temperature (top) and liquid nitrogen temperature (~ 100 K) (bottom). $Rb_2(TeBr_6)$ and $(NH_4)_2(TeBr_6)$ looked much like $Cs_2(TeBr_6)$ except in the IR where $(NH_4)_2(TeBr_6)$ showed ν_4 and ν_6 bands at low temperature.

C. Monoclinic $K_2(TeBr_6)$

At room temperature, hardly any noncubic features are present; the IR and Raman spectra have the usual three and four bands, respectively, characteristic of cubic $A_2(MX_6)$ crystals. This is consistent with the previous results.¹⁸⁻²² By cooling, there is a (reversible) gradual sharpening of the bands. The 53 cm^{-1} IR band is faintly observable at room temperature, and becomes increasingly distinct at lower temperatures. The 89 and 100 cm^{-1} IR bands can be weakly discerned around 200 K and are distinct only below $\sim 120\text{ K}$. The ν_4 band shifts gradually from ~ 100 to 110 cm^{-1} by the

cooling from 300 to 100 K . At low temperature ($\sim 120\text{ K}$), Adams *et al.*²⁰ observed ν_4 at $\sim 113\text{ cm}^{-1}$ and the bands at 78 and 55 cm^{-1} , but they did not resolve the sharp weak bands at 100 and 89 cm^{-1} .

No low temperature Raman results for $K_2(TeBr_6)$ have previously been reported. The broad bands at 99 and 92 cm^{-1} at room temperature (at 100 and 88 cm^{-1} according to Ref. 21) gradually sharpen into a triplet (111 , 103 , and 94 cm^{-1}), and weak but clearly real bands at 48 and 34 cm^{-1} appear at $\sim 100\text{ K}$.

There is an assignment problem with ν_5 . This mode

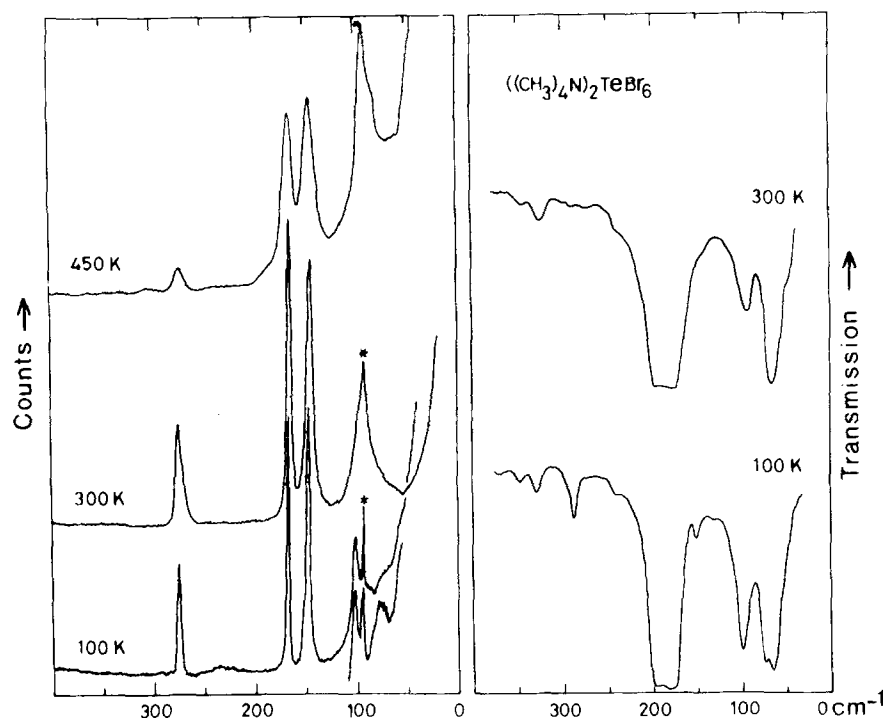


FIG. 4. $[(CH_3)_4N]_2(TeBr_6)$: Raman (left) and far IR spectra of powder samples¹ at the indicated temperatures. The spectra of $[(CD_3)_4N]_2(TeBr_6)$ were similar except for having a medium IR band at 380 cm^{-1} and no 287 cm^{-1} band at low temperature. The ν_3 CN symmetric stretching Raman active mode at 752 (hydrogen) and 678 cm^{-1} (deuterium) proved the identity of the samples and hence that the 275 cm^{-1} Raman bands are not methyl torsions. A laser plasma line is marked with asterisks.

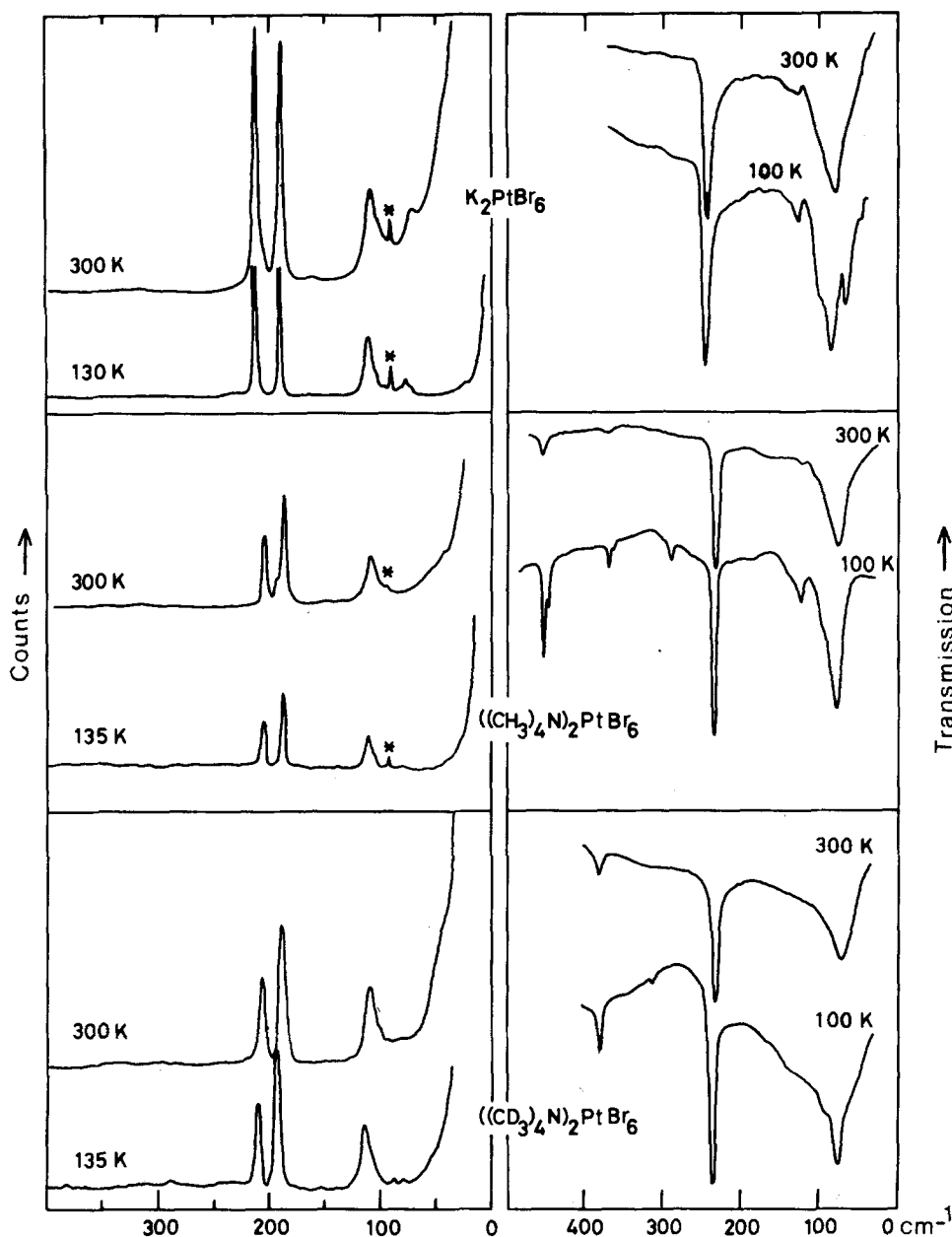


FIG. 5. Raman (left) and far IR spectra of powder samples¹ of hexabromoplatinates at the indicated temperatures. A laser plasma line is marked with asterisks.

has been observed near 70 cm^{-1} ^{18,22} in the Raman spectrum of aqueous solutions of $(\text{TeBr}_6)^{2-}$ and around 90 cm^{-1} in the Rb and Cs salts (Table III). An approximate formula derived by Yost *et al.*³⁵ estimates ν_5 of an octahedral $(\text{MX}_6)^{2-}$ ion as $[2/3(\nu_1^2 - \nu_2^2)]^{1/2}$. Thus, using 177 and 157 cm^{-1} for ν_1 and ν_2 , respectively, one gets a value of $\nu_5 = 67\text{ cm}^{-1}$, i.e., near the value in solution.

In $\text{K}_2(\text{TeBr}_6)$, Hendra and Zović¹⁸ identified Raman bands at 90 and 75 cm^{-1} as ν_5 and ν_{L2} , respectively. Adams and Morris,¹⁹ on the other hand, assigned ν_5 to their 73 cm^{-1} band but presumed that ν_5 and ν_{L2} interact due to identical symmetry so that a definite assignment is not possible. Creighton and Green²² took ν_5 to be split into bands at 85 and 70 cm^{-1} due to the monoclinic symmetry. Finally, Donaldson *et al.*²¹ assigned bands at 100 and 88 cm^{-1} to ν_5 , and the 78 cm^{-1} band was identified with perhaps ν_5 or ν_{L2} .

A consistent explanation appears to be that the bands at 99 , 92 , and 74 cm^{-1} contain a mixture of the "modes" ν_5 and ν_{L2} . Hence, the identifications in Table III ($\nu_5 = 99$ and 92 cm^{-1} and $\nu_{L2} = 74\text{ cm}^{-1}$) should not be taken rigorously; we merely estimate this to be the most predominant character of the bands.

The low temperature Raman bands at 48 and 34 cm^{-1} are assigned to ν_{L1} , the anion librations. Analogous bands occur in the low temperature phases of $\text{K}_2(\text{ReCl}_6)$, $\text{K}_2(\text{SnCl}_6)$, $\text{K}_2(\text{SnBr}_6)$, and $\text{K}_2(\text{TeCl}_6)$,^{36-40,1} e.g., in $\text{K}_2(\text{SnCl}_6)$, the (cubic) inactive $T_{1g}(\nu_{L1})$ rotatory mode of the $(\text{SnCl}_6)^{2-}$ octahedra becomes Raman active in the monoclinic phase (C_{2h}^5 ; below 255 K) and splits into two bands, observed at 46 and 38 cm^{-1} at 50 K .³⁷ In $\text{K}_2(\text{SnBr}_6)$, the bands occur at ~ 47 and $\sim 33\text{ cm}^{-1}$ at 100 K .³⁸⁻⁴⁰ The ν_{L1} bands in $\text{K}_2(\text{ReCl}_6)$, $\text{K}_2(\text{SnCl}_6)$, and $\text{K}_2(\text{SnBr}_6)$ have been shown^{38,37,39,40} to display "soft

TABLE III. Assignments and frequencies (cm^{-1}) of bands observed in $\text{A}_2(\text{MBr}_6)$. Underlined figures refer to ~ 100 K (Te) and ~ 135 K (Pt), and those in parentheses to 450 K.

	$\text{Rb}_2(\text{TeBr}_6)$	$\text{Cs}_2(\text{TeBr}_6)$	$(\text{NH}_4)_2(\text{TeBr}_6)$	$\text{K}_2(\text{TeBr}_6)$	$[(\text{CH}_3)_4\text{N}]_2(\text{TeBr}_6)$	$[(\text{CD}_3)_4\text{N}]_2(\text{TeBr}_6)$	$\text{K}_2(\text{PtBr}_6)$	$[(\text{CH}_3)_4\text{N}]_2(\text{PtBr}_6)$	$[(\text{CD}_3)_4\text{N}]_2(\text{PtBr}_6)$
Raman									
NH_4 bend.			1403, <u>1403w</u>		752 w	678 w			290 vw
C_4N sym. str. (ν_2^+)			312 wbr		275, 277 m	275 s			206, <u>210 s</u>
Combination					(274), 176, <u>177s</u>	168 s	213, <u>215 s</u>	204, <u>207 s</u>	186, <u>190 s</u>
$\nu_1(\text{MBr str.})$	179, <u>183 s</u>	174, <u>176 s</u>	178, <u>179 s</u>	176, <u>177s</u>	(166), 167, <u>169 s</u>	168 s	191, <u>193 s</u>	187, <u>188 s</u>	109, <u>112 s</u>
$\nu_2(\text{MBr str.})$	153, <u>157 m</u>	150, <u>152 m</u>	153, <u>155 s</u>	154, <u>157 s</u>	(145), 146, <u>149 s</u>	148 s	110, <u>114 w</u>	108, <u>113 m</u>	
$\nu_3(\text{MBr bend.})$	89, <u>89 s</u>	90, <u>90 s</u>	79, <u>81 s</u>	99, <u>111 wsh</u> 92, <u>103 m</u>	(~90), 93, <u>103 m</u>	91 s			
ν_{Lz} cation translation				94 wsh			73, <u>78 w</u>		87 vw 80 vw
ν_{Lz} anion rotation				74, <u>74 m</u>					
				48 w 34 w					
Infrared									
C_4N bend. (ν_3^+)						380, <u>380 m</u>		455, <u>453^a s</u>	381, <u>381 m</u>
C_4N bend. (ν_3^+)						344, <u>348 w</u>		370, <u>371^b w</u>	314 w
Combination					344, <u>347 w</u>	324, <u>328 w</u>			
Combination					323, <u>327 w</u>				
CH_3 tors. (ν_4^+)					287 m			292 w 183 vw	
CH_3 tors. (ν_4^+)									
Combination					240 vw				
$\nu_3(\text{MBr str.})$	~ 200 , <u>~ 205, vsbr</u>	~ 200 , <u>~ 203, vsbr</u>	~ 200 , <u>~ 204, vsbr</u>	195, <u>199 vsbr</u>	~ 183 , <u>~ 185, vsbr</u>	~ 185 , <u>~ 187, vsbr</u>	244, <u>247 vs</u>	233, <u>237 s</u>	233, <u>236 s</u>
ν_2			160 w		150 w	147, <u>150 w</u>			
$\nu_4(\text{MBr bend.})$			~ 118 , <u>~ 140, vsbr</u>	100, <u>110 m</u>	93, <u>97 s</u>	90, <u>94 s</u>	128 w	125 w	124 w
$\nu_6(\text{MBr bend.})$			50 w	53 w					
ν_{Lz} anion cation translation	55, <u>55 s</u>	56, <u>57 vs</u>	84, <u>106 m</u> 84, <u>84 s</u>	76s, <u>79 m</u> 89 w	64, <u>67 vs</u>	62, <u>66 vs</u>	80, <u>85 s</u> 68 w	76, <u>80 m</u>	71, <u>76 m</u>
Depicted in Fig.	3	3	3	3	4	5	5	5	5

^aAnother band occurs at 366 cm^{-1} .^bAnother band occurs at 448 cm^{-1} .

mode" behavior (i.e., having frequencies which depend markedly on the temperature). It was not possible with our equipment to detect any expected softening of the ν_{L1} bands in $K_2(\text{TeBr}_6)$.

At low temperatures, the *new* IR bands appearing at 100, 89, and 53 cm^{-1} deserve an explanation. The 53 cm^{-1} band was assigned as mainly ν_6 by Adams *et al.*,²⁰ based upon previous force field calculations on $(\text{TeBr}_6)^{2-}$.¹⁹ The approximate relationship $\nu_5 = \nu_6 \sqrt{2}$ gives $\nu_5 = 75 \text{ cm}^{-1}$ using $\nu_6 = 53 \text{ cm}^{-1}$, and this value of ν_5 is in reasonable agreement with the solution value of $\sim 70 \text{ cm}^{-1}$. We explain the weak bands at 100 and 89 cm^{-1} as components of ν_4 and ν_{L3} , these modes being split by the low symmetry (Table I).

In the monoclinic $K_2(\text{TeBr}_6)$ structure, the ν_{L1} rotatory modes are Raman allowed and the splitting of the ν_4 and ν_{L3} IR active modes takes place, already at room temperature (Table I). Hence, it is not possible to decide *whether* the appearance of the new bands in $K_2(\text{TeBr}_6)$ by cooling is caused by the normal sharpening of bands already weakly present (in conjunction with a gradually increasing distortion of the structure) *or whether* a further phase transition occurs somewhat above 120 K. The latter possibility might well be realized [cf. the five transitions in $K_2(\text{PtBr}_6)$, the four transitions in $K_2(\text{ReCl}_6)^{36}$ and the transition in monoclinic $K_2(\text{TeCl}_6)$ at $\sim 165 \text{ K}^1$]. The NQR data given by Nakamura *et al.*⁶ indicated a possible transition near 243 K. Further experiments, like NQR frequency data as a function of temperature, are needed to clarify the situation.

D. $[(\text{CH}_3)_4\text{N}]_2(\text{TeBr}_6)$

At room temperature, Adams and Morris¹⁹ identified ν_1 , ν_2 , ν_3 , and ν_5 modes at 170, 148, 180, and 96 cm^{-1} , and the IR bands at 104 and 68 cm^{-1} were thought to be mixtures of ν_4 and ν_{L3} . These results seem to be essentially correct. We observed the IR bands at 93 and 64 cm^{-1} and they both *shift* on deuteration.

Perhaps, the most remarkable observation (Fig. 4) is the Raman band at 275 cm^{-1} . A comparison of the $[(\text{CH}_3)_4\text{N}]_2(\text{TeBr}_6)$, $[(\text{CD}_3)_4\text{N}]_2(\text{TeBr}_6)$, and for example, $\text{Cs}_2(\text{TeBr}_6)$ spectra shows that the 275 cm^{-1} Raman band of the former compounds is not due to the $(\text{CH}_3)_4\text{N}$ ions: If it were a $(\text{CH}_3)_4\text{N}$ internal, it must be a methyl torsional mode by virtue of its low frequency²⁴ and hence it should suffer some deuteration shift, which it does not. Thus, we conclude that the band cannot be a methyl torsion (the observation of the polarized totally symmetric C_4N stretching mode ν_3^* at 752 cm^{-1} for the hydrogen compound and at 678 cm^{-1} for the deuterium compound proved the deuteration). On the other hand, if the 275 cm^{-1} Raman band is a mode characteristic of $(\text{TeBr}_6)^{2-}$, it should be observable in other $\text{A}_2(\text{TeBr}_6)$ salts. At first glance, this is not the case. The most reasonable explanation appears to be that the 275 cm^{-1} band is a second order feature of the internal motion of the $(\text{TeBr}_6)^{2-}$ ion, accidentally enhanced in these compounds. Binary combinations of the modes occurring near 185 and 90 cm^{-1} seem a likely way to fulfill the requirement of energy conservation ($93 + 183 = 276$ and $90 + 185 = 275 \text{ cm}^{-1}$; see Table III). Following these ideas, a very

weak band at 312 cm^{-1} in $(\text{NH}_4)_2(\text{TeBr}_6)$ can be explained as a combination of bands at ~ 200 and $\sim 118 \text{ cm}^{-1}$. The resonating combination in the tetramethylammonium compounds thus seems to be $\nu_3 + \nu_4$ rather than $\nu_3 + \nu_5$; ν_3 and ν_4 are *odd* modes forming *even* combinations, whereas a combination of ν_3 and ν_5 is *odd* and hence is not Raman allowed in a centrosymmetric crystal.

The weak IR features seem to origin from combinations of $\nu_1 + \nu_3$ (344 cm^{-1}), $\nu_2 + \nu_3$ or $\nu_5 + \nu_4$ (323 cm^{-1}), and $\nu_2 + \nu_4$ (240 cm^{-1}), all being of the type *even + odd = odd*.

The symmetry center of the crystal structure seems to be largely but not entirely conserved at low temperatures: It is difficult to explain the 150 cm^{-1} weak IR bands as anything except ν_2 . This applies also for the weak 160 cm^{-1} band of $(\text{NH}_4)_2(\text{TeBr}_6)$. Since the *even* ν_2 mode is IR forbidden under centrosymmetry, these crystals cannot strictly preserve their centrosymmetric structures at low temperatures, at least not on a time scale corresponding to an infrared experiment even though the time averaged structure as sampled using for example, x-ray diffraction methods might show centrosymmetry. Analogously, the $[(\text{CH}_3)_4\text{N}]_2(\text{PtCl}_6)$ x-ray crystal structure was shown to be centrosymmetric at room temperature,^{41,8} yet the vibrational spectra of the compound clearly indicated weak noncentrosymmetry (ν_2 and ν_3 were active in both IR and Raman).¹⁶ The noncentrosymmetry may be caused by a chirality of the tetramethylammonium ions (see Sec. V).

The presence of bands due to combinations in the spectra indicates anharmonicity. Normally, the anharmonicity of crystal modes increases with temperature because the larger population of thermal phonons in a hot crystal leads to enhanced phonon-phonon interaction. In the present case, the intensity of the anharmonicity allowed combination bands *decrease* with increasing temperature (Fig. 4), so that other effects than phonon populations must play a role. It is thought that the observed increase in anharmonicity at low temperatures might be accounted for by changes in the methyl torsional modes. These changes (Sec. V) in turn affect the $(\text{TeBr}_6)^{2-}$ vibrations because of the close methyl-bromine contacts in the crystal.⁶ In this way, an intensity trend opposite to that normally found can qualitatively be accounted for.

The methyl torsional modes within a $[(\text{CH}_3)_4\text{N}]_2(\text{MX}_6)$ crystal of $Fm3m$ symmetry are inactive.¹ The space group symmetry $Fd3c$ found for $[(\text{CH}_3)_4\text{N}]_2(\text{TeBr}_6)$, on the other hand, allows the methyl torsions to be IR and Raman observable *in theory* at room temperature (Table II), but *in practice* these bands are too weak and broad to be seen in the spectra at room temperature. We are sure about this because the spectra of the $[(\text{CH}_3)_4\text{N}]_2(\text{MB}_6)$ family of crystals are more easy to interpret than the corresponding hexachlorides. This is because the (MB_6) internals generally occur below 250 cm^{-1} , leaving the methyl torsional range around 300 cm^{-1} clean, whereas these two kinds of modes have similar energies in the hexachlorides.¹ There is therefore no doubt that the band observed at 287 cm^{-1} in IR at low temperatures (Table III) is due to a methyl group tor-

TABLE IV. Calculation of methyl torsional barrier heights in the threefold harmonic potential approximation. The overall moment of inertia of $(\text{CH}_3)_4\text{N}^+$ and the reduced methyl moment of inertia were taken to be 173×10^{-40} and $5.17 \times 10^{-40} \text{ g cm}^2$ giving an F parameter of 5.46 cm^{-1} .

Compound	Band (cm^{-1})	Torsional barrier $2K/9$		Methyl-methyl interaction $2L/9$		Mathieu barrier \bar{V}_3	
		cm^{-1}	kcal/mole	cm^{-1}	kcal/mole	cm^{-1}	kcal/mole
$[(\text{CH}_3)_4\text{N}]_2(\text{TeBr}_6)$	287	1806	5.2
$[(\text{CH}_3)_4\text{N}]_2(\text{PtBr}_6)$	292	1472	4.2	-263	-0.75	1904	5.4
	183					792	2.3
$[(\text{CH}_3)_4\text{N}]_2(\text{PtCl}_6)$	298 ^a	1620	4.6	-187	-0.54	1965	5.6
	228 ^a					1192	3.4
$(\text{CH}_3)_4\text{N NiCl}_3$	320 ^b	1994	5.7	-90	-0.28	2236	6.4
	291 ^b					1880	5.4

^aReference 1(b).

^bReference 44.

sional mode. We cannot exclude that the reason for the enhanced IR intensity at low temperatures might be a possible occurrence of a phase transition like the one observed in $[(\text{CH}_3)_4\text{N}]_2(\text{TeCl}_6)$,¹ but there was no abrupt change in the spectra at any particular temperature, so if any phase change is involved, it is a quite gradual one.

E. $\text{K}_2(\text{PtBr}_6)$

The room temperature spectra (Fig. 5) are in accordance with the cubic structure. Assigning the spectra presented no problem except for the ν_4 mode. Adams *et al.*^{25,28} assigned their 78 cm^{-1} IR band to ν_4 , whereas Hiraishi²⁸ and Hendra²⁹ took $\nu_4 = 90 \text{ cm}^{-1}$. In a more recent paper, Adams³¹ identified a band at 82 cm^{-1} as due to ν_4 as well as ν_{L3} . On the other hand, Debeau²⁷ held ν_4 to be unobserved due to accidental weakness and $\nu_{L3} = 85 \text{ cm}^{-1}$. Inspection of our temperature dependent IR spectra of $\text{K}_2(\text{PtBr}_6)$ (Fig. 5) in comparison to the tetramethylammonium compounds shows that ν_4 is in fact very weak at room temperature but can be observed near 125 cm^{-1} at $\sim 100 \text{ K}$. ν_4 was seen at 146 cm^{-1} in $(\text{NH}_4)_2(\text{PtBr}_6)$ ^{27,30} and an average value of 134 cm^{-1} was given for four $(\text{R}-\text{NH}_3)_2(\text{PtBr}_6)$ salts⁴² (R = methyl, ethyl, n -propyl, and isopropyl). Finally, the cation mass dependence of the $\sim 80 \text{ cm}^{-1}$ band (Table III) solves the assignment ambiguity: $\nu_4 \sim 128$ and $\nu_{L3} \sim 80 \text{ cm}^{-1}$ in $\text{K}_2(\text{PtBr}_6)$ at room temperature. Force field calculations and correlations of the bonding in the $(\text{PtBr}_6)^{2-}$ ion^{26,28,29,43} are of course more or less meaningless when based on erroneous assignment of ν_4 . Therefore, the calculations by Debeau and Poulet³⁰ should be considered the most reliable results to date on $(\text{PtBr}_6)^{2-}$.

Careful inspection of the low temperature spectra of $\text{K}_2(\text{PtBr}_6)$ shows indications of a decrease in crystal symmetry: The band shapes are not all symmetrical. ν_5 , ν_{L2} , and ν_{L3} seem to lose their threefold degeneracy, becoming split into site symmetry components. However, if we did not know in advance from the NQR and DTA results^{13,14} that transitions to lower symmetric phases occurred, we would not have been able to make it out with certainty. It must be concluded that the influence of the structural changes associated with the phase transitions at 169, 143, 137, and perhaps 105 K on the vibrational spectra is very modest.

F. $[(\text{CH}_3)_4\text{N}]_2(\text{PtBr}_6)$

Knowing the fundamental frequencies of the $(\text{PtBr}_6)^{2-}$, $[(\text{CH}_3)_4\text{N}]^+$, and $[(\text{CD}_3)_4\text{N}]^+$ ions from the literature, the spectra (Fig. 5) were easily assigned (Table III). The room temperature spectra yield no indication of any deviation from a cubic structure. At lower temperatures, methyl torsional bands gradually (and reversibly) appear, excluding a cubic $Fm\bar{3}m$ structure but not the $Fd\bar{3}c$ structure (Table II). Like for $[(\text{CH}_3)_4\text{N}]_2(\text{TeBr}_6)$ [and $(\text{CH}_3)_4\text{NNiBr}_3$ ⁴⁴], the sharpening of the methyl torsional bands is the more pronounced the lower the temperature, so that the possibility of the occurrence of phase transitions cannot be answered without further studies.

V. METHYL ROTATIONAL DISORDER IN $[(\text{CH}_3)_4\text{N}]_2(\text{MX}_6)$ SALTS

In a thermodynamic study, Pitzer⁴⁵ concluded that the methyl groups in the tetramethylmethane molecule [*neo*-pentane, isoelectronic with $(\text{CH}_3)_4\text{N}^+$] are prevented from rotating freely by a potential barrier of about 4.2 kcal/mole ($\sim 1470 \text{ cm}^{-1}$). More recent investigations using various experimental methods⁴⁶⁻⁴⁸ have confirmed this order of magnitude. The tetramethylammonium ion appears to have a higher barrier, around 6–7 kcal/mole, in its chloride, bromide, iodide, and hexafluorosilicate salts.⁴⁹⁻⁵⁵

Using the observed torsional frequencies and the formulas derived in previous papers,^{46,47} approximate barrier heights against methyl torsion can be estimated (Table IV). Here, a harmonic approximation to a threefold periodic potential was assumed,⁴⁷ and the eigenvalue parameters of the Mathieu equation were taken from Ref. 56. The approximation of a threefold barrier can be questioned but seems not to be too unreasonable.⁵³ From Table IV, average barrier heights of the order of 4 to 5 kcal/mole are obtained. With such barrier heights, the methyl groups will largely be confined to restricted torsional oscillations around their C–N axes, and will not be pseudo-freely rotating. This point was not adequately stressed in our previous papers,^{16,42} which considered the freezing out of either “essentially free” methyl rotation or some kind of methyl group disordering as explanations for the gradual appearance of

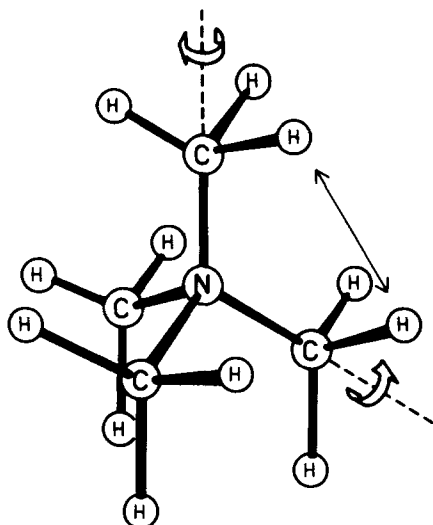


FIG. 6. The tetramethylammonium ion in the *staggered* conformation. Arrows indicate how small rotations increase the nonbonded intermethyl H-H distance.

methyl torsional bands at lower temperatures. The barrier heights in Table IV show that this explanation must be modified: The methyl groups do not perform essentially free rotation even at room temperature ($kT \sim 0.6$ kcal/mole at 300 K).

Consider a physical "ball and stick" model of the tetramethylammonium ion (Fig. 6). The charge distribution within the ion presumably leaves the hydrogens somewhat positive such that nonbonded hydrogen-hydrogen repulsions can be expected from one methyl group to the other (intermethyl H-H distance ~ 2.5 Å). This is the physical basis for the torsional potential barrier in the isolated ion. From the model or Fig. 6, it can be seen that the two high-symmetric *staggered* and *eclipsed* conformations of the ion (both having $T_d = \bar{4}3m$ symmetry) are unstable from the point of view of minimizing the nonbonded intermethyl H-H repulsions. Starting from the *all-staggered* conformation, it is found that if the methyl groups are rotated slightly in the *same sense* (i.e., all clockwise or all counterclockwise around the C-N bond), then all the nonbonded intermethyl H-H distances increase. A minimum in the potential energy probably occurs near a rotation by $\sim 10^\circ$ ⁵⁷ from the *staggered* conformation (a 60° rotation would create the *eclipsed* conformation). The symmetry of the ion in the potential energy minimum conformation is $T=23$. Hence, enantiomorphism occurs.

The potential barrier between "right-handed" and "left-handed" conformations seems to be quite small. This means that at room temperature there is probably an essentially free rotatory oscillation within $\pm 20^\circ$ from the *staggered* conformation. Furthermore, a certain proportion of the ions probably have one of its methyl groups in the *eclipsed* conformation, since (as the model or Fig. 6 shows) if three methyls in the ion are *staggered*, then the fourth appears to be quite stable as *eclipsed*. A similar conclusion has been obtained quantitatively for the *neo*-pentane molecule.⁵⁸ The *eclipsed* methyl group can of course be any of the four ones.

Hence, we have several possible methyl-orientational disordering mechanisms in tetramethylammonium crystals. We expect that this disorder smears out the methyl torsional bands and breaks the crystal translational symmetry, so that phonons from throughout the Brillouin zone become weakly spectroscopically active. The bands may become so broad that they disappear in the background. As the crystal is cooled, the thermal motion is slowed down, gradually producing clusters of higher order and giving the observed reversible sharpening of the methyl torsional bands. A variety of increasingly ordered phases may in principle be formed. Phase transitions have indeed been observed in the majority of the examined tetramethylammonium compounds: in hexahalo-metallates,^{1,59} trihalometallates,^{44,60} hexahydrohexaborate,⁶¹ chlorate,⁶² and in the chloride.^{52,63-66}

VI. CONCLUSIONS

It appears from this study that it is possible to observe and detect phase transitions in $A_2(MX_6)$ crystals using the method of variable temperature vibrational spectroscopy. However, in several cases $[(NH_4)_2(TeBr_6)]$, $K_2(TeBr_6)$, and $K_2(PtBr_6)$, the effects observed were weak and it must be concluded that transitions exist [like those in $K_2(PtBr_6)$] which produce very little change in the spectra.

For the tetramethylammonium compounds studied, the possibility of the occurrence of methyl rotational order-disorder type transitions is quite realistic. Other methods, like NQR, DTA, etc. are needed to describe the situation in detail.

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- ¹(a) R. W. Berg, F. W. Poulsen, and N. J. Bjerrum, J. Chem. Phys. **67**, 1829 (1977); (b) R. W. Berg, J. Chem. Phys. **69**, 1325 (1978).
- ²I. D. Brown, Can. J. Chem. **42**, 2758 (1964).
- ³A. K. Das and I. D. Brown, Can. J. Chem. **44**, 939 (1966); **47**, 4288 (1969); L. M. Manojlovic, Chem. Abstr. **52**, 2494 (1958).
- ⁴K. W. Bagnal, R. W. M. D'Eye, and J. H. Freeman, J. Chem. Soc. **1955**, 3959.
- ⁵J. E. Fergusson and P. F. Heveldt, Aust. J. Chem. **27**, 661 (1974).
- ⁶D. Nakamura, K. Ito, and M. Kubo, J. Am. Chem. Soc. **84**, 163 (1962).
- ⁷T. C. Gibb, R. Greatrex, N. N. Greenwood, and A. C. Sarma, J. Chem. Soc. A **1970**, 212.
- ⁸R. W. Berg and K. Nielsen, Acta Chem. Scand. (accepted) and unpublished results.
- ⁹R. H. Busch, E. E. Galloni and C. R. Haitz, Struct. Rep. **15**, 160 (1951); A. G. Sharpe, J. Chem. Soc. **1953**, 4177.
- ¹⁰D. H. Brown, K. R. Dixon, C. M. Livingston, R. H. Nuttall, and D. W. A. Sharp, J. Chem. Soc. A **1967**, 100.
- ¹¹H. D. Grundy and I. D. Brown, Can. J. Chem. **48**, 1151 (1970).
- ¹²D. Nakamura, Y. Kurita, K. Ito, and M. Kubo, J. Am. Chem. Soc. **82**, 5783 (1960).
- ¹³H. M. van Driel, M. Wiszniewska, B. M. Moores, and R. L. Armstrong, Phys. Rev. B **6**, 1596 (1972); R. L. Armstrong, J. Magn. Reson. **20**, 214 (1975).

- ¹⁴K. Rössler and J. Winter, *Chem. Phys. Lett.* **46**, 566 (1977).
- ¹⁵M. Wiszniewska and R. L. Armstrong, *Can. J. Phys.* **51**, 781 (1973).
- ¹⁶D. Nakamura and M. Kubo, *J. Phys. Chem.* **68**, 2989 (1964).
- ¹⁷N. N. Greenwood and B. P. Straughan, *J. Chem. Soc. A* **1966**, 962.
- ¹⁸P. J. Hendra and Z. Jović, *J. Chem. Soc. A* **1968**, 600.
- ¹⁹D. M. Adams and D. M. Morris, *J. Chem. Soc. A* **1967**, 2067.
- ²⁰D. M. Adams, J. D. Findlay, M. C. Coles, and S. J. Payne, *J. Chem. Soc. Dalton Trans.* **1976**, 371.
- ²¹J. D. Donaldson, S. D. Ross, J. Silver, and P. J. Watkiss, *J. Chem. Soc. Dalton Trans.* **1975**, 1980.
- ²²J. A. Creighton and J. H. S. Green, *J. Chem. Soc. A* **1968**, 808.
- ²³D. J. Stufkens, *Rec. Trav. Chim.* **89**, 1185 (1970).
- ²⁴R. W. Berg, *Spectrochim. Acta Part A* **34**, 655 (1978).
- ²⁵D. M. Adams and H. A. Gebbie, *Spectrochim. Acta* **19**, 925 (1963).
- ²⁶J. Hiraishi, I. Nakagawa, and T. Shimanouchi, *Spectrochim. Acta* **20**, 819 (1964).
- ²⁷M. Debeau and M. Krauzman, *C. R. Acad. Sci. Ser. B* **264**, 1724 (1967).
- ²⁸D. M. Adams and D. M. Morris, *J. Chem. Soc. A* **1967**, 1666.
- ²⁹P. J. Hendra, *Spectrochim. Acta Part A* **23**, 2871 (1967); P. J. Hendra and P. J. D. Park, *Spectrochim. Acta Part A* **23**, 1635 (1967).
- ³⁰M. Debeau and H. Poulet, *Spectrochim. Acta Part A* **25**, 1553 (1969).
- ³¹D. M. Adams and S. J. Payne, *J. Chem. Soc. Dalton Trans.* **1974**, 407.
- ³²D. Breittinger, G. Bauer, W. Haegler, L. Emmert, and W. Kress, *Proceedings of the Sixth International Conference on Raman Spectroscopy*, edited by E. D. Schmid, R. S. Krishnan, W. Kiefer, and H. W. Schrötter (Heyden, London, 1978), Vol. II, p. 318.
- ³³A. Ries, *Z. Kristallogr.* **49**, 513 (1911).
- ³⁴H. Marshall, *Inorganic Syntheses* (McGraw-Hill, New York, 1946), Vol. II, p. 189.
- ³⁵D. M. Yost, C. C. Steffens, and S. T. Gross, *J. Chem. Phys.* **2**, 311 (1934).
- ³⁶G. P. O'Leary and R. G. Wheeler, *Phys. Rev. B* **1**, 4909 (1970), and references therein.
- ³⁷J. Pelzl, P. Engels, and R. Florian, *Phys. Status Solidi B* **82**, 145 (1977); J. Winter, K. Rössler, J. Bolz, and J. Pelzl, *Phys. Status Solidi B* **74**, 193 (1976).
- ³⁸J. W. Anthonsen, *Acta Chem. Scand. Ser. A* **28**, 974 (1974).
- ³⁹B. I. Swanson, *Phys. Status Solidi A* **47**, K95 (1978).
- ⁴⁰J. Pelzl (personal communication).
- ⁴¹R. W. Berg and I. Sjötofte, *Acta Chem. Scand. Ser. A* **32**, 241 (1978).
- ⁴²J. B. Perison and W. B. White, *Spectrochim. Acta Part A* **33**, 487 (1977).
- ⁴³P. Labonville, J. R. Ferraro, M. C. Wall, S. M. C. Basile, and L. J. Basile, *Coord. Chem. Rev.* **7**, 257 (1972).
- ⁴⁴R. W. Berg and S. Skaarup, *J. Phys. Chem. Solids* **39**, 1193 (1978).
- ⁴⁵K. Pitzer, *J. Chem. Phys.* **5**, 473 (1938); *Discuss. Faraday Soc.* **10**, 66 (1951).
- ⁴⁶J. R. Durig, S. M. Craven, and J. Bragin, *J. Chem. Phys.* **52**, 2046 (1970).
- ⁴⁷S. Weiss and G. E. Leroi, *Spectrochim. Acta Part A* **25**, 1759 (1969).
- ⁴⁸C. I. Ratcliffe and T. C. Waddington, *J. Chem. Soc. Faraday Trans. 2* **72**, 1821 (1976).
- ⁴⁹J. Dufourcq and B. Lemanceau, *J. Chim. Phys.* **67**, 9 (1970).
- ⁵⁰M. Mahajan and B. D. N. Rao, *J. Phys. Chem. Solids* **33**, 2191 (1972).
- ⁵¹S. Albert, H. S. Gutowsky, and J. A. Ripmeester, *J. Chem. Phys.* **56**, 3672 (1972).
- ⁵²A. A. V. Gibson and R. E. Raab, *J. Chem. Phys.* **57**, 4688 (1972).
- ⁵³C. I. Ratcliffe and T. C. Waddington, *J. Chem. Soc. Faraday Trans. 2* **72**, 1935 (1976).
- ⁵⁴H. Rager and A. Weiss, *Z. Phys. Chem. NF* **93**, 299 (1974).
- ⁵⁵H. Rager and A. Weiss, *Ber. Bunsenges. Phys. Chem.* **82**, 535 (1978).
- ⁵⁶J. R. Durig, M. S. Craven, and W. C. Harris, *Vibrational Spectra and Structure*, edited by J. R. Durig (M. Dekker, New York, 1972), Vol. 1, p. 73.
- ⁵⁷In *neo*-pentane, a minimum near a rotation of $\sim 7^\circ$ has been found numerically by an empirical force field [S. Melberg and K. J. Rasmussen (to be published)].
- ⁵⁸E. N. Lassetre and L. B. Dean, *J. Chem. Phys.* **17**, 317 (1949).
- ⁵⁹W. von der Ohe, *J. Chem. Phys.* **63**, 2949 (1975).
- ⁶⁰P. S. Peercy, B. Morosin, and A. G. Samara, *Phys. Rev. B* **8**, 3378 (1973).
- ⁶¹R. Schaeffer, Q. Johnson, and G. S. Smith, *Inorg. Chem.* **4**, 917 (1965).
- ⁶²T. Kiichi, M. Nomoto, N. Nakamura, and H. Chihara, *Phys. Status Solidi A* **41**, K17 (1977).
- ⁶³S.-S. Chang and E. F. Westum, *J. Chem. Phys.* **36**, 2420 (1962).
- ⁶⁴M. Stämmler, *J. Inorg. Nucl. Chem.* **29**, 2203 (1967).
- ⁶⁵J. Dufourcq, Y. Haget-Bouillaud, N. B. Chanh, and B. Lemanceau, *Acta Crystallogr. Sect. B* **28**, 1305 (1972).
- ⁶⁶C. W. F. T. Pistorius and A. A. V. Gibson, *J. Solid State Chem.* **8**, 126 (1973).